

The University of Chicago

A STUDY OF THE SPECTRAL
PHOTOELECTRIC RESPONSE OF
SOLUTIONS OF SODIUM IN
LIQUID AMMONIA

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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By
GEORGE MICHAEL SCHMEING

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INTRODUCTION

Previous investigations concerning the photoelectric properties of ammonia solutions of alkali metals include the work of Kraus¹ which reported some evidence of a photoelectric effect, that of Chittum and Hunt² reporting that there was no effect, and that of Crapple³ who demonstrated finally that there is an effect.

In this present work "monochromatic" light was used. The currents were measured with an electrometer and the relative flux of the light was found with a thermopile-galvanometer. The ratio of the electrometer deflection to the galvanometer deflection will be termed the response. The results are shown by curves for solutions of sodium in liquid ammonia at several concentrations and at different temperatures.

¹J. Am. Chem. Soc., 43, 749 (1921).

²J. Phys. Chem., 40, 581 (1936).

³Unpublished dissertation, University of Chicago, 1933.

APPARATUS

The photocell, Figures 1 and 2, was constructed of pyrex glass. The window was of quartz, the collecting ring of platinum, and the metal contacts sealed into the glass were tungsten. The cap was made of a commercial ground glass joint of standard type. The light source used was a quartz arc similar to that employed by Young and Pierce⁴ which was a modification of that described by Forbes and Harrison.⁵ Two heavy duty 45 volt "B" batteries supplied voltage for the photocell. Two other batteries, in a separate circuit, furnishes the potential for the electrometer needle. The wire connecting the photocell to a Dolezalec electrometer was double cotton covered copper wire impregnated with paraffin and threaded through paraffin coated tubes of pyrex glass which were supported coaxially in one inch brass tubing by paraffined corks. Contact was made with the photocell through mercury in tubes L and N, Figures 1 and 2, by means of nickel-tipped, copper wires.

The Dolezalec electrometer was equipped with a gold sputtered quartz fibre suspension. The quartz was drawn in a brush, rustling, oxygen-"natural gas" flame. The fibres were caught on a piece of dark colored velvet. After the fibres were graded for size and uniformity under a microscope, they were sputtered with gold. The electrometer circuit used was an adaptation of the circuit and method of operation employed by Zscheile, Hogness and Young.⁶ The electrometer switch is illustrated in Figure 3. The thermal and electrical electrometer shield was equipped with a plate glass window and an intake for air through a calcium chloride drying tower. The sensitivity of the electrometer was such that 4.4×10^{-14} ampere caused a deflection of 0.1 cm. on the scale 2.5 meters away.

The monochromator was the quartz instrument used and described by Young and Pierce.

⁴J. Optical Soc. Am., 21, 498 (1931).

⁵Rev. Sci. Instruments, 11, 99 (1925).

⁶J. Phys. Chem., 38, 3 (1934).

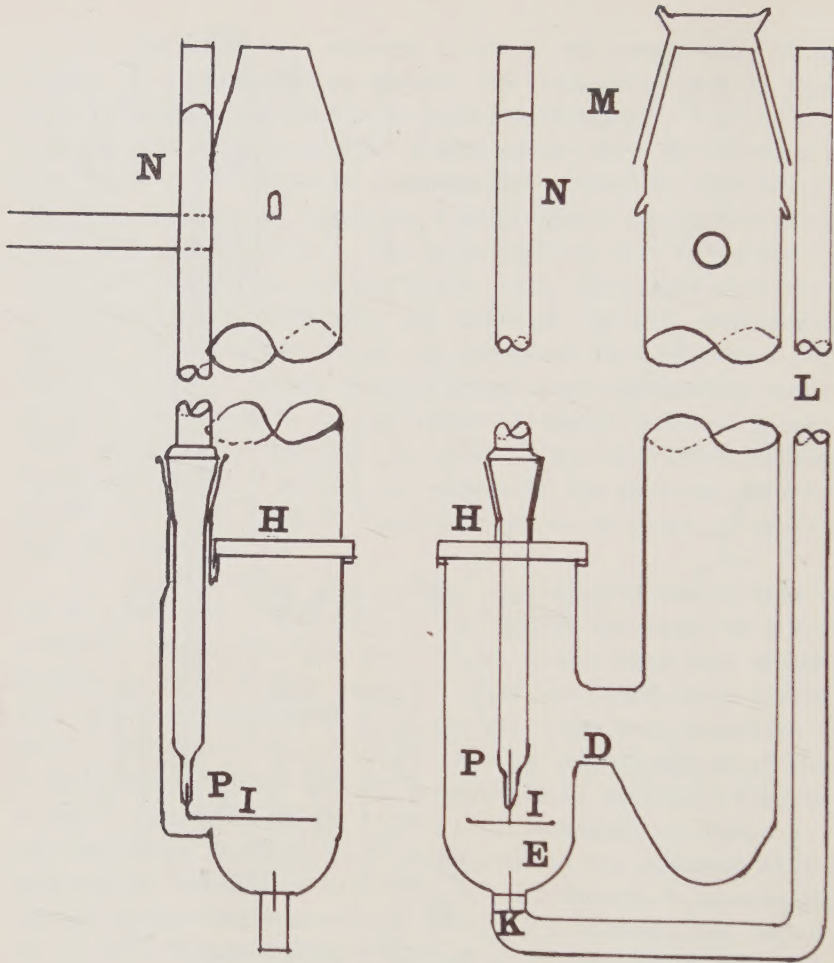


Fig. 2.--Photocell detail

- M Standard taper cap.
- N Paraffined tube of pyrex glass. This tube contains mercury in its lower portion to make electrical contact with the platinum loop "I" through the tungsten "P."
- L A tube similar to "N" affording electrical contact with the solution in "E" through tungsten "K."
- H Quartz window.
- D Barrier

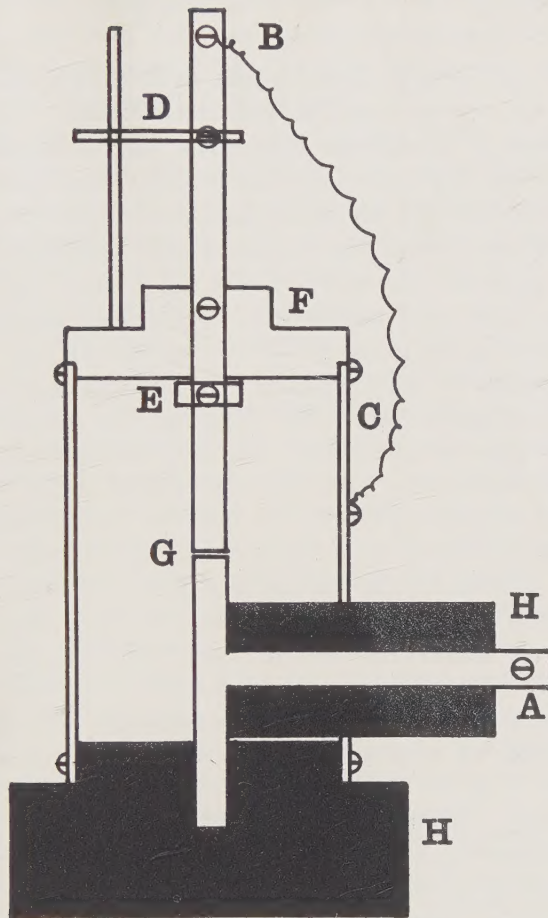


Fig. 3.--Detail of electrometer switch

- A Connection to quadrant pair.
- B Grounded connection, a brass rod capable of vertical motion, operated by a linen cord running over glass pulleys to operator at telescopes and switchboard.
- C Grounded brass shield.
- D Fork, traveling over guide, to prevent rotation of rod "B."
- E Collar to limit vertical motion of rod "B."
- F Brass cap drilled to accommodate rod "B" and permit its vertical motion.
- G Platinum contacts.
- H Insulating material.

PROCEDURE

A small glass ampule with a long capillary neck was blown to the proper size, cooled, and weighed. A piece of sodium was placed in a vertical test tube, and the ampule was inserted in an inverted position over the sodium. The test tube was evacuated. The sodium was melted by means of a stearic acid bath. Dry air, admitted to the test tube through anhydrous calcium chloride and phosphorous pentoxide, drove the molten sodium through the capillary neck into the ampule. The filled ampule was weighed and placed in position at "A" in one end of the tube, "AB," Figure 1 attached to the photocell. A glass weight was placed in the opposite end at point "B." During this operation tube "AB" was in a horizontal position. The cell was evacuated until no current leak across the cell was observable. Then the cell was turned to a vertical position so that the glass weight fell upon the ampule and broke it. Further pumping removed any gases occluded by the sodium.⁷ The vacuum line with its attached storage bulbs was filled to atmospheric pressure with ammonia from a small steel bottle containing sodium wire. From the measured volume of the line and the barometric pressure the amount of ammonia was determined. By means of a counterbalanced carriage running on vertical guides, an acetone carbon dioxide bath⁸ in a silvered dewar was

⁷During the first few experiments dry hydrogen was used to force the molten sodium into the ampule but this was abandoned in favor of dry air. When hydrogen was used, much pumping was necessary to re-evacuate the cell after breaking the ampule. J. W. Mellor (*Modern Inorganic Chemistry*, Longmans, Green & Co., New York, 1925, p. 420) states that sodium occludes twenty times its own volume of hydrogen.

⁸When an acetone carbon dioxide bath is prepared, the solid carbon dioxide is usually allowed to sink in the acetone. The room is then filled with dangerous and disagreeable acetone vapor because carbon dioxide gas is blown through the acetone. To avoid this hazard, a convenient amount of commercial acetone was poured into the dewar and a block of solid carbon dioxide was suspended in it by means of a wire mesh supported just below the surface of the acetone. The solution was stirred by convection currents produced by the settling of the cooler, denser portion. When no more solid carbon dioxide appeared to dissolve, powdered carbon dioxide was stirred into the solution with a wooden dowel

slowly raised about the lower part of the photocell. Ammonia condensed on the sodium. The resulting solution was stirred by motion of the cell, and when the solution was thoroughly mixed, it was decanted over the barrier, "D," between the mixing chamber, "A," Figure 1, and the photocell proper, "E."

The mercury arc was started. The prisms of the monochromator were adjusted till the desired line of the mercury arc was coincident with a reference line on a target of uranium glass which had previously been lined up with the exit slit of the monochromator. The entrance slit was closed until the spectral lines observed on the uranium glass screen no longer overlapped. The exit slit was closed until only the desired line left the instrument. The observing lens system and the uranium glass bearing the target were removed; the light was brought to fall on the blackened surface of a thermopile⁹ and connected to a galvanometer¹⁰ and the resulting galvanometer deflection was recorded. The thermopile was racked out of the optical path and the beam, traced by fluorescent screens in the ultra violet, reflected from the aluminium-vaporized-on-glass mirror through the quartz window and thence through the platinum loop was brought onto the surface of the solution. The electrometer deflection was recorded. The thermopile-galvanometer was again read at this time, and the pressure within the cell was recorded (Tables 1 and 2). When the electrical and optical measurements were completed, the ammonia was drawn off through a measured amount of sulphuric acid and the excess acid titrated with sodium hydroxide. A mixture, half petroleum ether and half 95 per cent ethyl alcohol, was poured into the cell to remove the sodium residue. Aliquots of this solution were titrated with standard sulphuric acid.

That the currents recorded in the tables were actually due to photoelectric properties of sodium in liquid ammonia was

rod. An additional block of solid carbon dioxide was then placed in the solution to maintain the temperature, which was observed by means of a pentane thermometer.

⁹The thermopile (Kipp and Zonen) is an eighteen-element instrument with a 6 mm. blackened receiver mounted behind a quartz window. The measured resistance of the thermopile is 31 ohms.

¹⁰The galvanometer (Leads and Northrup, H.S.) is of copper coil, copper suspension, and copper contact construction with a resistance of sixteen ohms and a critical damping resistance of 30 ohms.

demonstrated as follows. 1. The residue in the cell was irradiated after the ammonia had been boiled off. No measurable photo-current resulted. 2. The cell was filled with ammonia, ammonium salts and with mixtures of these materials. The empty cell as well as the cell with the various contents produced no electrometer deflection when irradiated. Only solutions of sodium in ammonia gave a response. 3. The potential drop across the photocell was reversed and was shown to prevent the flow of the photoelectric current.

If, while the potential on the cell was reversed, light struck the platinum loop in the cell, there was a slight movement of the electrometer. Therefore, by means of a quartz lens, the beam of light was brought to a focus at the approximate center of the platinum collector ring in the cell to avoid illuminating the ring itself in all of the electrical measurements described.

RESULTS

Experiment 1. Spectral response curves. Table 1 compares two runs on the same photocell.

TABLE 1

Run	Wave-length in Å	Galv. De- flect.	Elec. De- flect.	Elect. Deflect.		Dev. from Mean	Photo- current Amps $\times 10^{13}$	Electrons per Photon
				Galv. Deflect.	Mean			
A	3125	1.35	2.40	1.78			10.6	.0316
B	..	1.35	2.40	1.78	1.78	...	10.6	.0316
A	3650	4.17	6.00	1.44			26.4	.0219
B	..	4.10	6.05	1.48	1.46	.02	26.4	.0225
A	4046	1.50	2.60	1.73			11.4	.0237
B	..	1.50	2.60	1.73	1.73	...	11.4	.0237
A	4358	3.10	2.20	0.710			9.68	.0280
B	..	3.10	2.20	0.710	0.710	...	9.68	.0280
A	5460	1.88	2.30	1.22		.07	10.1	.0234
B	..	1.90	2.05	1.08			9.02	.0208
C	..	1.82	2.10	1.15	1.15		9.24	.0213
A	5790	1.28	1.10	0.859		.15	4.84	.0105
B	..	1.21	1.40	1.16	1.01		6.16	.0134
								.0232 (av.)

Max. 26.4×10^{-13}

Min. 4.84×10^{-13}

Table 2 gives responses of a similar cell over a greater range of wavelengths.

TABLE 2

Wavelength in Å	Response in arbitrary units	
	<u>Electrometer Deflection</u>	<u>Galvanometer Deflection</u>
2224	10.00	
2378	3.90	
2536	1.33	
2893	0.67	
3125	1.78	
3650	1.44	
4046	1.73	Violet
4358	0.71	Blue
5460	1.17	Green
5790	1.01	Yellow
(7000	0.18	Red)

The data of Table 2 are plotted in Figure 4.

Temp: Room 27 to 26° C; Bath: -82 to -70° C.

Pressure: Barometer, 751.1 uncorrected; Line, 8.5 m.m. Hg at -82° C; 9.5 m.m. Hg at -70° C.

Light: Quartz capillary arc, 110 volts, D.C., 2.5 amps.

Electrometer: 1 cm = 4.4×10^{-13} amps.

Galvanometer: 1 cm = 1.4×10^{-8} amps.

Volume of line: 6760 ml.

The volume of the line without the photocell was found in three ways.

Method 1. The outside dimensions were measured by calipers and a meterstick. The wall thickness was taken from tables supplied by the Corning Glass Works. From these data the volume was computed to be 6365 ml.

Method 2. The volume of a two "liter" bulb was measured by filling it with water. This bulb was then dried and attached to the line through a glass stopcock. When the line was filled with air, the pressure was recorded. The stopcock was closed. The line was evacuated. The pressure was recorded. The stopcock was opened. The pressure was again recorded. From these pressure readings and the volume of the bulb, the volume of the line was calculated by Boyle's Law to be 6301 ml.

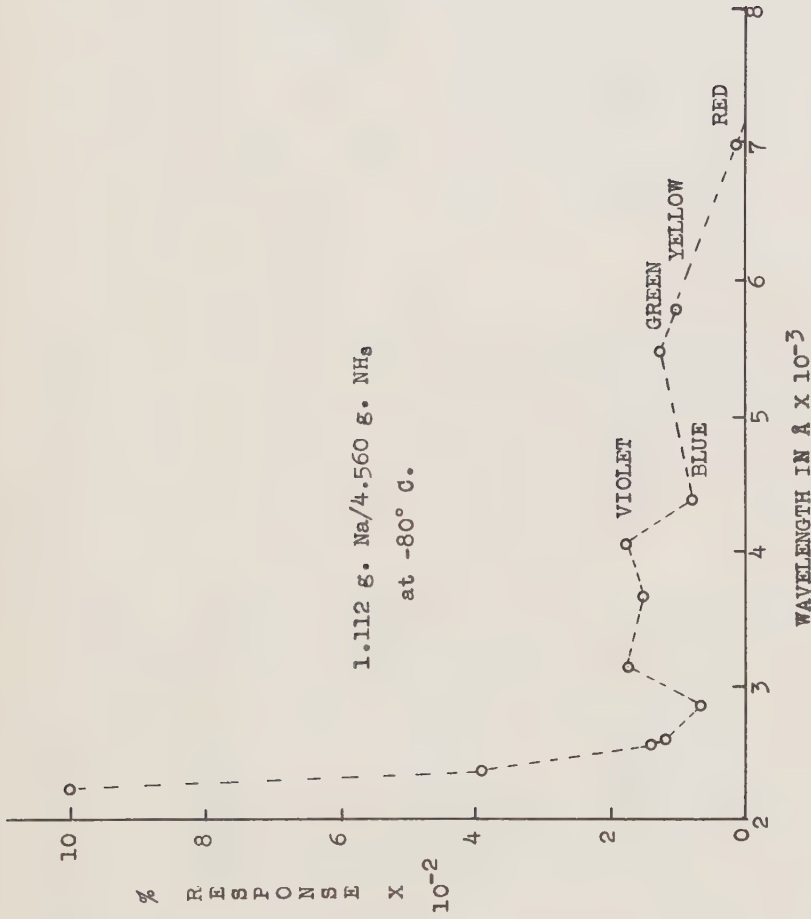


FIG. 4

Method 3. The line was filled with ammonia. The pressure was recorded. The ammonia was withdrawn through an excess of twice normal sulphuric acid and from the titration values; the volume of the line was calculated to be 6358 ml.

The photocell was filled with water to determine the volume, 395 ml.

From the volume of the line, the weight of the ammonia used in these experiments was determined to be 4.560 g. per run.

The quantity of sodium used in Experiment 1, Table 1, found by weighing was 1.1118 grams; by titration 1.112 grams.

(In a different experiment the weighing gave 1.0934 g. and two titrations gave 1.090 and 1.084 g.)

Concentration: 1.112 g. sodium in 4.560 g. ammonia.

Color of Solution: Red bronze. -

The observation marked 7000 was made with a tungsten filament source.

Experiment 2. Effect of concentration.

In Figure 5, the spectral response curves of two solutions of different concentrations are plotted on the same coördinates to show relationships.

Experiment 3. Effect of color of solution.

TABLE 3*

Wavelength in Å	Response of Blue Bronze Solution Arbitrary Units	Response of Red Bronze Solution Arbitrary Units
4046 Violet	0.96	2.36
4358 Blue	1.00	0.85
5460 Green	0.61	3.39
5790 Yellow	0.79	1.65
6907 Red	(0.00)	1.03

*The data of Table 3 are shown in Figure 6.

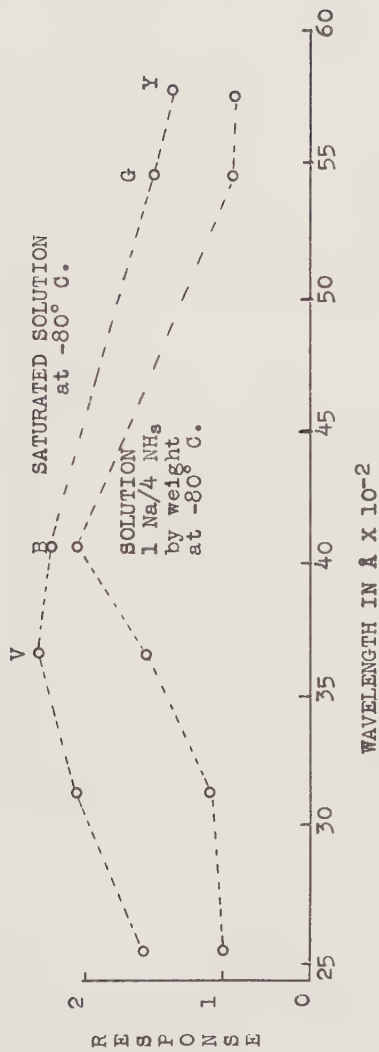


Fig. 5

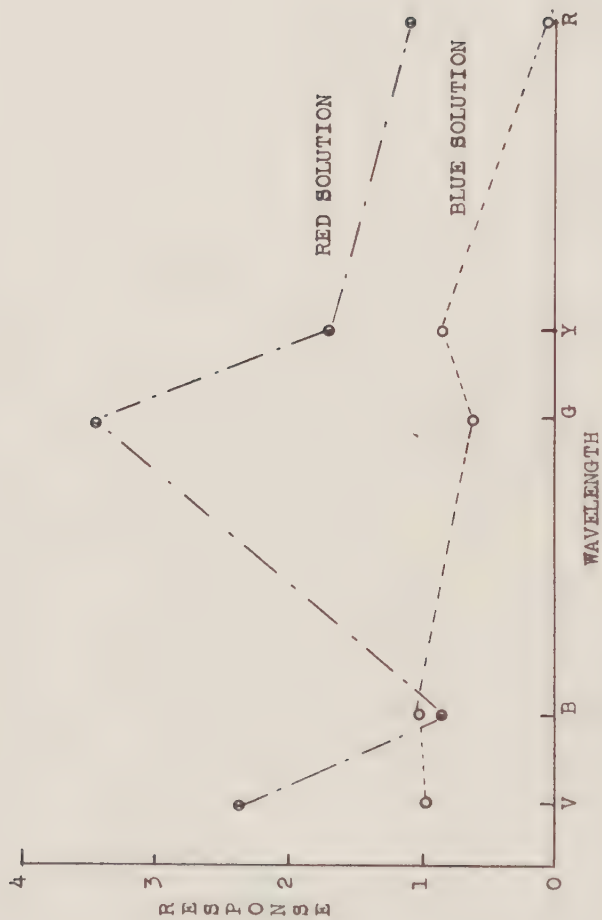


FIG. 6

Experiment 4. Effect of temperature. (Pressure?)

TABLE 4*

Wavelength in Å	Response			
	Blue Bronze		Red Bronze	
	-46°C	-80°C	-65°C	-80°C
2536	..	..	1.40	1.00
3125	..	..	1.90	1.20
3650	..	..	1.60	1.60
4060 Violet	..	..	1.50	2.10
4358 Blue	1.30	1.00	1.45	1.85
5460 Green	0.70	0.61	0.90	0.90
5790 Yellow	..	..	0.70	0.90
6907 Red	..	..	0.10	0.20

*The data of Table 4 are shown in Figure 7.

Summary and Discussion of Results

While light from a quartz capillary arc was passed through a monochromator onto the surface of a solution of sodium in liquid ammonia raised to a negative potential, a platinum ring above the surface of the solution collected photoelectrons. A Dolezalek electrometer indicated the potential drop across a high resistance through which the photocurrent was conducted and a thermopile-galvanometer measured the light flux. The quotient, electrometer reading / galvanometer reading, was plotted as ordinate against the wavelength of the radiation incident on the surface of the sodium-in-ammonia solution.

In experiment 1a measurements were made with light ranging from 3125 to 5790 Å in wavelength. The maximum photocurrent of 26.6×10^{-13} ampere was obtained with light of wavelength 3650 Å and the minimum, 4.84×10^{-13} ampere, at 5790 Å. The average number of photoelectrons per photon was .0232.

In experiment 1b the range of measurement extended from 2224 to 7000 Å. The maximum response was at 2224 and the threshold is apparently just beyond 7000 Å.

The points on the curve, Figure 4, are connected by a dashed straight line rather than by a smooth curve because more points are needed before it will be possible to give the exact

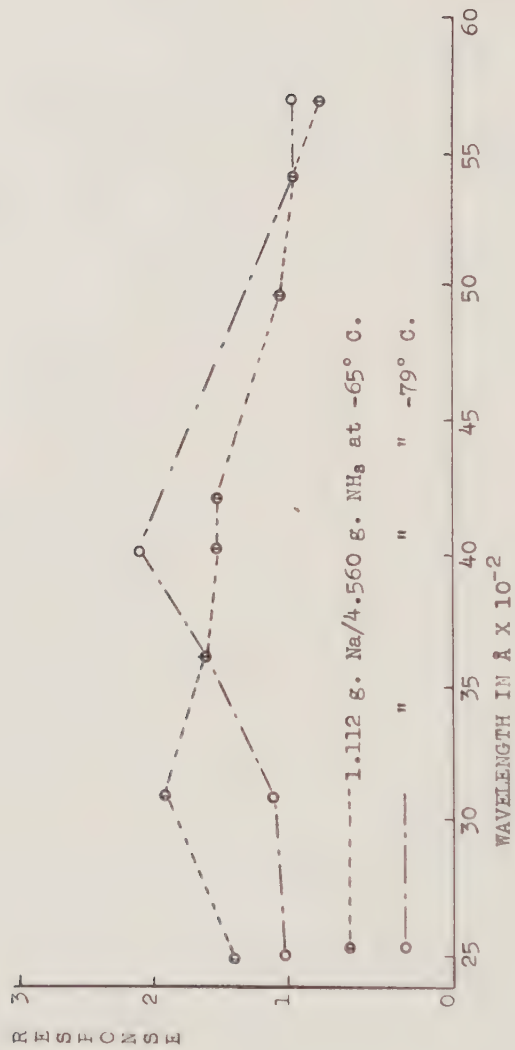


Fig. 7

shape of the curve.

In Experiment 2 the response of a solution of one gram of sodium in four grams of ammonia was compared with that of a saturated solution over the range 2536 to 5790 Å. Within the region studied, the more concentrated solution gives the greater response. This generalization is in keeping with semi-quantitative observations made throughout this work. The maximum response of the saturated solution was at 3650 and that of the other was at 4046 Å.

In Experiment 3 the responses of a red and of a blue solution were compared. The maxima in the spectral response curves occurred at wavelengths roughly corresponding to the complementary colors of the solutions.

In Experiment 4 measurements were made at -65° C. and at -80° C. An increase in temperature shifted the maximum toward the violet. The variation may be due to a change in pressure above the solution or a change in the vapor pressure of the solution or to both of these causes acting simultaneously. A change in the character of the solution may be at the bottom of this observation. It is too early to attempt a theoretical explanation of the observations made in Experiment 4 and recorded in Figure 7.

ACKNOWLEDGMENT

I wish to take this opportunity to express my appreciation of the invaluable encouragement, guidance, and advice given by Dr. T. F. Young in connection with this problem.

